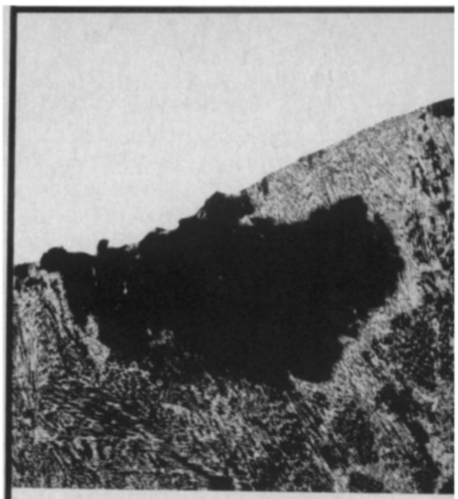
The Bugs of Rust

Researchers are trying to tease out how microorganisms influence the corrosion of metals

By JANET RALOFF

Copious deposits of iron bacterium Hyphomicrobium sp. *along welds in stainless steel nuclear-powerplant piping. Under deposits are deeply corroded pits.*

Pope/RPI



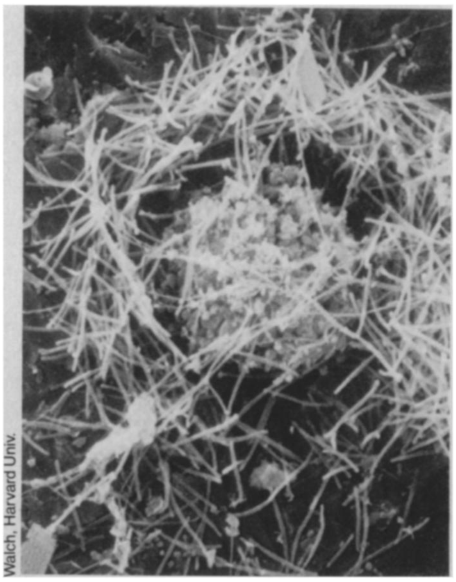
Cross-section of stainless steel weld showing deep pit (black region) that developed under bacterial deposit. Corroding biota tend to prefer colonizing welds.

Pope/RPI

It is common practice to test new piping and chemical tanks for leaks by filling them with water and then watching what happens. At a facility in Victoria, Tex., the plant managers chose to conduct this hydrostatic testing using local well water. Any water clean enough to drink, they reasoned, was also clean enough to run through the system. After the stainless steel piping and tanks passed the tests, the chemical tanks were drained but the piping wasn't. Shortly thereafter, a hurricane threat prompted the plant managers to refill the chemical tanks with water ballast against the storm.

"The first indication of a problem was water dripping from butt welds in brand new stainless steel piping," recalls Gregory Kobrin, a materials engineer with E.I. duPont de Nemours in Beaumont, Tex. Perplexed about what could have gone wrong, workers opened up a tank too. Most of the tank's water had evaporated, leaving behind a silty mess and series of curious looking 4-inch-diameter mounds arranged along a weld at the bottom. Poking one of the inflamed-looking protuberances, engineers spotted a pit at the edge of the weld. X-ray examination of the spot later showed that the pinhole surface breach gave way to a cavernous pit underneath. In the nodules along the weld were communities of bacteria, feeding on the products of corrosion.

Kobrin wasn't the first to recognize the symbiotic relationship that many types of bacteria, algae and fungi have with corroding metals. But his experience typifies what a growing number of plant and pipeline engineers throughout the world are confronting: unexpected and rapid corrosion in the presence of microorganisms.



Walch, Harvard Univ.

Seven days after exposure to seawater, metal surface had acquired this nest of rod-like bacteria, which already housed a different microflora inside.

Each year metal corrosion in the United States alone does about $167 billion worth of damage — from rusting of culverts to the weakening of bridges and perforation of oil pipelines and industrial storage tanks for hazardous chemicals. According to Ray G. Kammer, deputy director of the National Bureau of Standards (NBS) in Gaithersburg, Md., "A good portion of the [corrosion] is biologically induced."

Ironically, the magnitude of this microbially influenced corrosion is barely recognized outside the fledgling research community investigating it, notes Steve Dexter, a University of Delaware at Lewes researcher who chaired at NBS last month the first U.S. conference focusing on the subject.

People have been studying aspects of biocorrosion since at least 1934, when a landmark paper was published by a Dutch research team. It proposed an electrochemical process to explain the corrosion of pipes in anaerobic (oxygenless) soils by sulfate-reducing bacteria (SRBs).

However, Dexter told SCIENCE NEWS, even 10 years ago, "a meeting like this would have been impossible." Particularly in the United States, he says, and to a lesser extent elsewhere, the mainline corrosion community had not yet come to accept the concept that biology could significantly influence the chemistry of corrosion. The reason, he said, is that while bacteria were frequently associated with sites of active corrosion, there was little proof that they had caused the corrosion or were even influencing it.

But as last month's meeting showed, things are changing. To begin with, its sponsors were two bastions of the mainline corrosion-engineering community — NBS and the National Association of Corrosion Engineers. More important, the research results presented not only firmed up earlier charges against sulfate-reducing bacteria but also identified a growing list of previously unindicted coconspirators.

Corrosion, in what is known as an anodic reaction, involves the movement of metal from a surface into a solution as an electrically charged species. This process leaves electrons behind on the surface. Acids and other corroding compounds contain hydrogen ions (H^+), each of which is short one electron. When they contact an anodic metal surface, these acids will steal some of the excess electrons, generating hydrogen gas (H_2). This movement of electrons from a surface to hydrogen ions in the acids sets up a detectable electric current.

Brenda Little of the Naval Ocean Research and Development Activity laboratory in Mississippi, set out to measure what share of any corrosion that was observed in the presence of microorganisms was actually being caused by those organisms. To do this she placed identical metal samples into separate water baths. The pieces of metal, which serve as two electrodes in a circuit, were connected by a zero-resistivity ammeter to measure any current flow between them. If corrosion was occurring at the same rate on the metal in each water-bath system, the net current flow between them would be zero. But if the corrosion rate was higher in one system, the magnitude and direction of the current flow attributable to it would be detected by the ammeter.

In one test, Little used aerobic (oxygen-dependent) filamentous bacteria that had been isolated and cultured from a brazed nickel joint that failed unexpectedly in high-temperature corrosion tests. One sterile nickel sample was inoculated with the bacteria; the other remained bacteria-free. When the samples were placed in their respective water baths and allowed to corrode, the bacterial system showed an excess corrosion rate of 1.6 milli-inches per year, an indication of the corrosion's growth, or penetration, rate.

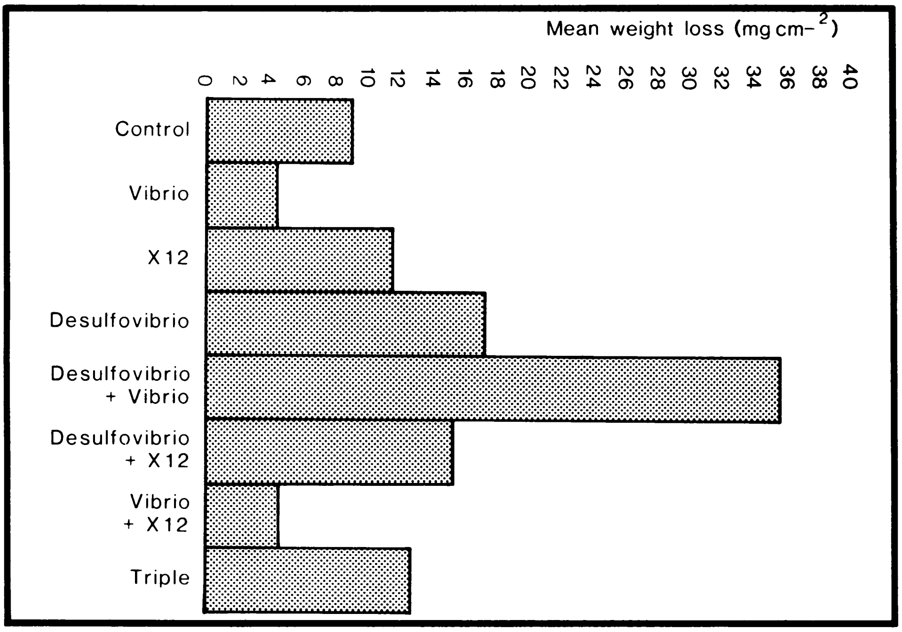
Little was able to identify three microbial factors influencing the corrosion rate: metabolic production of two corrosion-enhancing materials — isobutyric and isovaleric acids; a higher rate of oxygen aeration; and the microorganisms' ability to secrete extracellular polymers capable of trapping metals (such as iron) from the ambient water flowing through their environment.

Though Little's work is one of the more convincing indictments of bacterial involvement, it employed only single strains of aerobic microorganisms. Research by Christine Gaylarde and her colleagues at the City of London Polytechnic in England reflects a more complex chain of interrelated mechanisms that exist in the real world.

Work by Gaylarde and J. Johnston, for example, has shown that while the bacterium *Vibrio anguillarum* has no corrosive abilities of its own (and in fact can act as a mild inhibitor of corrosion), its presence can enhance corrosion associated with the notorious sulfate-reducing bacterium *Desulfovibrio vulgaris*. Curiously, however, *Vibrio* also reduces the normal corrosivity associated with the hydrogen-sulfide-producing bacterium that Gaylarde calls X12 (probably *Citrobacter*).

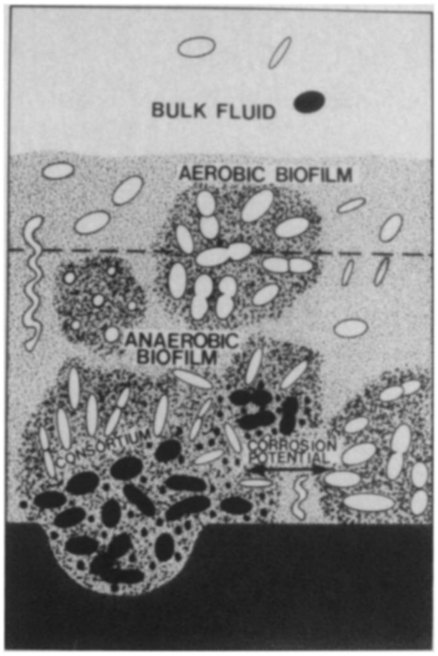
Gaylarde speculates that the *Vibrio* may form a tightly bound coating when it attaches to a metal — in this case steel — somehow protecting it from dissolving. In fact, she and Johnston speculate that the increased corrosion seen when *Vibrio* and *Desulfovibrio* cohabit a metal sample could be a result of this developing "biofilm" trapping *Desulfovibrio* cells.

More paradoxical, Gaylarde says, is the low corrosion rate that occurs when all three bacteria jointly colonize a piece of steel. However, if X12 has some influence on how the others interact, she says, then the mere presence of an SRB like *Desulfovibrio vulgaris* does not necessarily indicate a potential corrosion problem.



Gaylarde

Dramatic differences in biocorrosion can occur within three weeks —as measured in mean weight loss of the affected metal —when bacteria colonize steel alone or in the company of others. Species used came from London-area estuary.



J. W. Costerton, Univ. of Calgary

Chemical changes associated with environment under neighboring corrosive consortia on metal (black area) may actually enhance corrosion rate at each site.

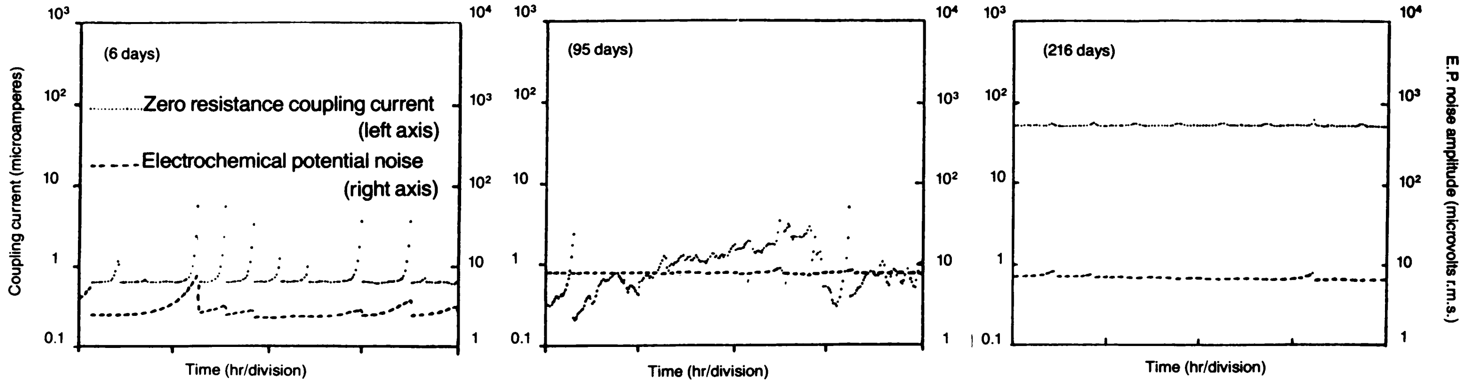
Other work on biofilms suggests that the first microbial settlers onto a vulnerable metal surface are likely to be aerobes; they'll put down "roots" to anchor their community to a metal surface. As in the situation Kobrin described, the anchoring settlement may be a tubercle produced by iron-oxidizing bacteria. Alternatively, it could be a mat of interlaced filaments generated by other bacteria. Over time different species will be attracted to the community — because of the nutrients their neighbors provide, or, in a water environment, for the protection their settlement affords from strong currents. Eventually a slimy biofilm encapsulates this diverse and thriving community.

Though sulfate-reducing bacteria can survive in an aerobic environment, they thrive and produce copious amounts of corrosive hydrogen sulfide gas only in an anaerobic environment. W.A. Hamilton of the University of Aberdeen in Scotland says it's possible that early SRB pioneers of a metal-adhering community will bide their time until the biofilm gets thick enough (perhaps only 10 to 25 microns thick) to turn its environment anaerobic. By that point, he notes, conditions should have turned ideal "for the growth of the obligately anaerobic sulfate-reducing bacteria, with all the attendant problems of sulfide production and corrosion."

To Hamilton that suggests a likely layered stratification among organisms dwelling in mature biofilm communities. In the uppermost stratum at the water-biofilm boundary are aerobes, whose vigorous use of oxygen helps to foster an anaerobic environment in the biofilm beneath them. Feeding on the by-products of their metabolism is a mid-level community of anaerobes. The fermentation products they generate in turn feed sulfate reducers at the metal surface.

Supporting this model is new research suggesting that many newly identified sulfate-reducing bacteria thrive on foods they were previously thought to shun, including acetate, carbon dioxide and propionate — chemicals the mid-tier anaerobes might well generate.

What few corrosion engineers, even mi-



Electrochemical signatures (from techniques pioneered at University of Manchester) for ductile iron under attack in aqueous SRB environment. At 6 days, (above left), each spike in zero resistance current signals temporary break in metal's protective ("passive") surface film, allowing corrosion. By 95 days (center graph), current suggests low-level ongoing corrosion. Potential noise (low frequency variations in current) signals that nonprotective iron/iron-sulfide film has replaced passive film. By 216 days, sulfide film is still stable. Current indicates there is also stable high rate of corrosion. Graphs: King/UMIST

crobiologists, appreciate today, Hamilton says, is that active SRBs depend on their biofilm neighbors to help maintain the nutrition and environment necessary for them to produce hydrogen sulfide (H_2S). Moreover, though there are many chemical biocides that will kill free-swimming sulfate-reducing bacteria, few of these biocides are able to penetrate mature biofilms well enough to reach those SRBs that pose the greatest corrosion threat.

Controlling sulfate-reducing bacteria in Britain's offshore oil industry is the focus of a pioneering biocorrosion research program at the University of Aberdeen, on the North Sea. When the program began there about seven years ago, explains microbiologist Peter Sanders, it dealt with biocorrosion of external surfaces on drilling and oil storage platforms. "Very rapidly, however, we realized that the major corrosion problem was in production systems — pipelines, oil storage tanks, the water injection system [that pumps water into oil reservoirs to maintain pressure as the oil is removed] and systems for cleaning up oily water." This kind of corrosion is already severe, Sanders says, requiring constant and very costly replacement or maintenance of those affected systems, like pipes, that are serviceable.

Because of the relative invulnerability of sulfate-reducing bacteria within biofilms, Sanders says, "we've got a major effort under way on finding ways to remove film." One such program involves adding detergents and surface-active compounds to try to penetrate and chemically remove existing films. They are also investigating techniques for oxygenating water systems; the idea is that if one can prevent anaerobic microenvironments from developing, the SRBs won't get a chance to begin generating sulfides. The problem is that any region where water flow is not rapid could be turned anaerobic if a biofilm is allowed to form. Finally, the program is investigating new biocides and biocide application strategies.

A new technique, which these researchers call radiorespirometry, makes possible quick evaluation of the success of such programs. Samples of water, metal or any other substance contaminated with sulfate-reducing bacteria are placed in test tubes along with radioactively tagged sodium sulfate — food for the SRBs. By analyzing how much sulfate has been converted to radioactively tagged sulfide, researchers are able to assess within a day the sulfide-generating capacity of the sampled system.

Because few plant engineers are sufficiently trained in microbiology to identify the bacteria they find associated with corrosion, efforts are getting under way to develop rapid diagnostic field kits. For example, under contract to the Materials Technology Institute of the Chemical Process Industries, Dan Pope at Rensselaer Polytechnic Institute in Troy, N.Y., is developing systems that use enzyme dyes linked to antibodies against particular microbes for a rough-cut gauge of contamination. Color intensity — indicating how many of a particular type of microbe were in a cultured sample — is visually matched against a color key. Another set of diagnostic techniques involving fluorescent staining of microbial antibodies allows the counting of actual organisms in a sample. Though these require a microscope for viewing, they permit finer resolution of the level of contamination and identification of "bugs."

In England, at the University of Manchester's Institute of Science and Technology, researchers are using innovative electrochemical techniques such as current noise and potential noise to study how microbes promote corrosion. Current noise measures fluctuations in the corrosion current between two pieces of metal to establish how the rate of corrosion at a particular site varies over time. Potential noise involves charting spikes in the electrical potential of a corroding metal in solution. Normally, corrosive spot pitting would go undetected without visual inspection, explains Roger King, a director of Corrosion Protection Centre Industrial Services (a commercial enterprise of the university). But each spike identifies the point at which the natural protective sulfide coating on a metal breaks down, allowing further corrosion to occur.

By coupling these techniques in an analysis of biocorrosion of cast iron pipes in soil, King is studying the mechanism of corrosion initiation. The original oxide skin that forms on a metal, the "passive" surface, normally prevents further corrosion of a surface. But as microbes produce iron sulfide in the soil around a cast iron surface, he says, the passive film starts to break down — evidenced by a spike, or blip, in the surface's potential noise. Immediately the oxide coating reforms. But under continued attack by the microbes that can convert ferrous iron (Fe^{2+}) into ferric iron (Fe^{3+}), King says, the metal's passive skin begins to change into a different oxide — this one with a larger surface area that can no longer comfortably match the surface area of the metal under attack. The result is that this new oxide skin bulges and cracks. And at each crack, an anodic site develops where corrosion occurs.

The hope is that field engineers can one day harness techniques such as these to identify problems in their initial stages, before those metals under bioattack have been degraded beyond repair. Until then, however, corrosion engineers must learn to devise protective strategies based on observation and microbiological cunning.

Along those lines, several scientists attending the NBS meeting shared some of their observations on what works (for example, periodic scraping of metal surfaces to remove building biofilms) and what to look out for (epoxy pipe coatings, whose pigments offer gourmet fare for hungry microbes). But the real key to managing the problem, most participants emphasized, is first to acknowledge that biocorrosion is a threat, and then to gear everything from plant design to testing and maintenance toward making metal surfaces as inhospitable and inaccessible to microbes as possible. ☐